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COMPUTATIONAL ANALYSIS OF SOME ASPECTS OF A
SYNTHETIC ROUTE TO AMMONIUM DINITRAMIDE

by

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13. ABSTRACT (Maximum 200 words)

The optimized geometry of 1, $C_2H_5-O-\overset{O}{\overset{\|}{C}}-N(NO_2)_2$, a precursor to ammonium dinitramide, has been computed at the *ab initio* HF/6-31G* level. We find no structural evidence that 1 exists in the ionic form, $C_2H_5-O-C\equiv O^+ \; N(NO_2)_2^-$. The reaction of 1 with NH_3 passes through a transition state that is consistent with a concerted substitution (Ingold mechanism) in which $N(NO_2)_2^-$ is the leaving group.

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Introduction

Eq. (1) shows the final step in a synthetic route to ammonium dinitramide:

$$C_2H_5-O-\overset{\overset{\textstyle O}{\|}}{C}-N(NO_2)_2 \quad \xrightarrow{2\ NH_3} \quad C_2H_5-O-\overset{\overset{\textstyle O}{\|}}{C}-NH_2 \quad + \quad NH_4^+\,N(NO_2)_2^- \qquad (1)$$

1   **2**
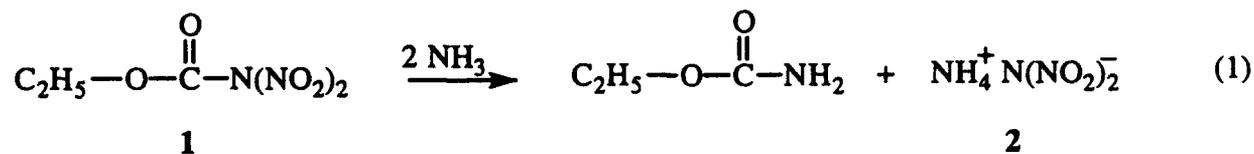
In this work, we have addressed two questions:

(1) Is there any evidence to indicate that **1** may actually be in the ionic form **1B**?

$$C_2H_5-O-C\equiv O^+ \quad N(NO_2)_2^- \qquad\qquad \textbf{1B}$$

(2) Does eq. (1) proceed through the tetrahedral intermediate (or transition state) **3**, or is it a concerted substitution (Ingold mechanism) which goes through the transition state **4**, with $N(NO_2)_2^-$ being the leaving group?

$$C_2H_5-O-\overset{\overset{\textstyle O^-}{|}}{\underset{\underset{\textstyle +NH_3}{|}}{C}}-N(NO_2)_2 \qquad\qquad\qquad C_2H_5-O-\overset{\overset{\textstyle O}{\|}}{\underset{\underset{\textstyle NH_3}{\vdots}}{C}}\cdots N(NO_2)_2$$
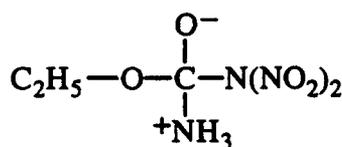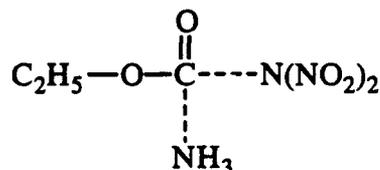
3   **4**

Methods

All geometries were optimized at the *ab initio* HF/6-31G* level, using the GAUSSIAN 92 code [1]. The HF/6-31G* vibration frequencies were calculated for each structure, in order to determine whether it corresponds to a local energy minimum (zero imaginary frequencies) or to a transition state (one imaginary frequency).

Results and Discussion

Figure 1 shows our computed structure for **1**. It has no imaginary frequencies, confirming that it corresponds to an energy minimum. The C=O and C–N(NO$_2$)$_2$ distances are quite reasonable for these types of bonds at the HF/6-31G* computational level [2], and do not support

the idea that **1** may be in the form **1B**, for which one would anticipate an anomalously short C=O bond and long C–N(NO$_2$)$_2$. Furthermore, when we attempted to compute an optimized geometry for the cationic portion of **1B**, treating it as a separate entity, it broke up into CO$_2$ and C$_2$H$_5^+$.

Our calculated structure for the transition state in eq. (1), formed by allowing NH$_3$ to interact with the central carbon in **1**, is given in Figure 2. It is indeed a transition state (not an intermediate), with one imaginary frequency corresponding to a vibrational mode involving the C–NH$_3$ and C–N(NO$_2$)$_2$ bonds. The bond angles around the central carbon are 100.6, 102.4, 117.0 and 125.1 degrees; these indicate a significant deviation from tetrahedral symmetry, for which they would all be 109.5°. In addition, the C=O distance (1.201 Å) is only 0.027 Å longer than in **1** and is quite compatible with this still being a double bond, whereas structure **3** suggests a single bond. On the other hand, the C–N(NO$_2$)$_2$ bond length has increased to 1.660 Å, compared to 1.450 Å in **1**. The C–NH$_3$ distance is almost as great, 1.615 Å. All of these results indicate that structure **4** is a better representation of the transition state than is **3**, despite many examples of nucleophilic interactions with carboxyl derivatives proceeding by tetrahedral mechanisms [3,4].

An interesting feature of the transition state is a hydrogen bond between an ammonia hydrogen (H$_{21}$) and a nitro oxygen (O$_9$), as indicated by the dashed line in Figure 2. The H$_{21}$···O$_9$ distance is 2.093 Å. For that nitro group, the N–NO$_2$ distance is 1.366 Å, which is less than the 1.414 Å - 1.423 Å range of the other N–NO$_2$ bonds in **1** and **4**. As the incipient C–NH$_3$ bond becomes shorter and stronger, H$_{21}$ may migrate to O$_9$, forming an isomer of dinitraminic acid which could subsequently react with a second NH$_3$ to give the product, ammonium dinitramide (**2**).

References

[1] GAUSSIAN 92, Revision C, M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1992.

[2] W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, Ab Initio Molecular Orbital Theory, John Wiley and Sons, New York, 1986.

[3] S. J. Weininger and F. R. Stermitz, Organic Chemistry, Internat. Ed., Academic Press, New York, 1984, section 17:5.

[4] J. March, Advanced Organic Chemistry, 3rd. ed., Wiley-Interscience, New York, 1985, ch. 10.

Bond Lengths (Å)

O 1– C 2	1.292
O 1– C 3	1.443
C 2– O 4	1.174
C 2– N 5	1.450
C 3– C12	1.511
C 3– H13	1.080
C 3– H14	1.080
N 5– N 6	1.414
N 5– N 7	1.417
N 6– O 8	1.180
N 6– O 9	1.176
N 7– O10	1.175
N 7– O11	1.183
C12– H15	1.084
C12– H16	1.083
C12– H17	1.083

Bond Angles (deg)

|		
C 2– O 1– C 3	117.2
O 1– C 2– O 4	129.4
O 1– C 2– N 5	108.4
O 1– C 3– C12	107.0
O 1– C 3– H13	107.9
O 1– C 3– H14	108.0
O 4– C 2– N 5	122.2
C 2– N 5– N 6	114.3
C 2– N 5– N 7	116.1
C12– C 3– H13	112.5
C12– C 3– H14	112.3
C 3– C12– H15	109.3
C 3– C12– H16	110.8
C 3– C12– H17	110.8
H13– C 3– H14	108.9
N 6– N 5– N 7	112.5
N 5– N 6– O 8	117.2
N 5– N 6– O 9	113.6
N 5– N 7– O10	114.9
N 5– N 7– O11	116.2
O 8– N 6– O 9	129.2
O10– N 7– O11	128.9
H15– C12– H16	108.6
H15– C12– H17	108.5
H16– C12– H17	108.8
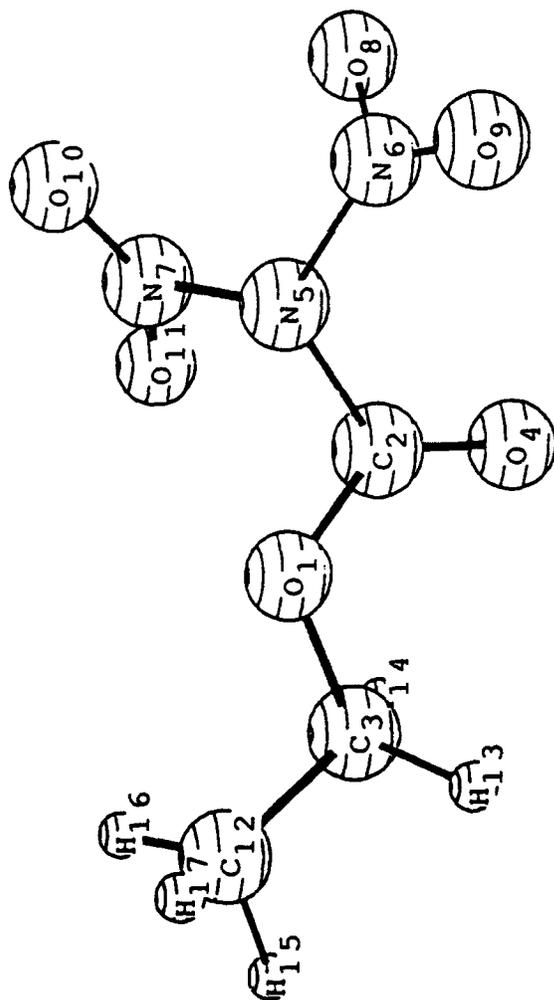
FIGURE 1. HF/6-31G* optimized geometry of 1.

FIGURE 2. HF/6-31G* optimized geometry of transition state.

Bond Lengths (A)

O 1- C 2	1.350
O 1- C 3	1.436
C 2- O 4	1.201
C 2- N 5	1.660
C 2- N18	1.615
C 3- C12	1.513
C 3- H13	1.082
C 3- H14	1.077
N 5- N 6	1.366
N 5- N 7	1.423
N 6- O 8	1.182
N 6- O 9	1.198
N 7- O10	1.180
N 7- O11	1.183
C12- H15	1.085
C12- H16	1.083
C12- H17	1.084
N18- H19	1.006
N18- H20	1.007
N18- H21	1.009

Bond Angles (deg)

C 2- O 1- C 3	116.3
O 1- C 2- O 4	125.1
O 1- C 2- N 5	100.6
O 1- C 2- N18	102.4
O 1- C 3- C12	106.9
O 1- C 3- H13	108.6
O 1- C 3- H14	109.0
O 4- C 2- N 5	117.0
O 4- C 2- N18	111.9
N 5- C 2- N18	95.0
C 2- N 5- N 6	115.6
C 2- N 5- N 7	112.9
C 2- N18- H19	112.6
C 2- N18- H20	106.9
C 2- N18- H21	107.3
C12- C 3- H13	111.8
C12- C 3- H14	111.9
C 3- C12- H15	109.7
C 3- C12- H16	110.6
C 3- C12- H17	111.1
H13- C 3- H14	108.5
N 6- N 5- N 7	110.5
N 5- N 6- O 8	119.3
N 5- N 6- O 9	114.3
N 5- N 7- O10	114.9
N 5- N 7- O11	117.4
O 8- N 6- O 9	126.3
O10- N 7- O11	127.7
H15- C12- H16	108.5
H15- C12- H17	108.4
H16- C12- H17	108.5
H19- N18- H20	110.0
H19- N18- H21	110.3
H20- N18- H21	109.7